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(54) [発明の名称] 超分枝状ポリマー

(57) [要約]

本発明は、少なくとも30000の重量平均分子量を有する超分枝状ポリマーの製造法であって、少なくとも3つの官能性末端基を有する第1プレポリマーおよび少なくとも2つの官能性末端基を有する第2プレポリマーを、これらのプレポリマーの該末端基の間の脱水縮合反応によって結合させることを含む該製造法に関する。本発明によれば、官能化プレポリマーのアーム数および/または分子量を正確に調整することができるので、得られる超分枝状ポリマーの特性を所望の方法で変性させることができる。また、随意に別の化学反応に使用することのできる超分枝状ポリマー中の官能性末端基の数は容易に所望のレベルまで調整することができる。高い分子量を有する超分枝状ポリマーは、有機溶剤またはカップリング化合物を使用することなく、高収率で製造することができ、このことは、環境的な見地および経済的な見地から有利である。

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[Field of the Invention]

[0001]

This invention relates to letter polymer of super-branching of letter (hyperbranched) polymer of super-branching, the biodegradability which has the weighted mean molar mass (molar mass) of at least 30000 especially, and/or hydrolysis nature, and a manufacturing method for the same.

[0002]

The term of "the letter of super-branching" is a term known by the person skilled in the art of the field concerned. This term includes the polymer which has 1 or two or more central atoms as a branching off point which many polymer chains (namely, arm) combine rather than two or it which is constituted by each repeating unit. Since these arms have an additional branching off point, in the polymerization continued further, a possibility of advancing branch and/or bridge construction further is brought about.

[Background of the Invention]

[0003]

It is known that the polymer which has high molar mass, especially poly (hydroxycarboxylic acid) (lactic acid), for example, poly, cannot be prepared by a direct dehydrating condensation reaction. It originates in the balance between the chemical species in a reaction mixture, and polymer of low molar mass with a poor mechanical property is often obtained to many uses. Chemical concern for solving this problem is increasing from a viewpoint of the consciousness of an environmental problem. Some trials for manufacturing the polymer which has molar mass high enough, for example, poly etc., (hydroxycarboxylic acid) are made.

[0004]

In European Patent application gazette EP-A-0572675, the method of manufacturing resolvability poly (hydroxycarboxylic acid) polymer with high molar mass by a dehydrating condensation reaction is indicated. :polyisocyanate compound in which the method of manufacturing poly (hydroxy acid) polymer by making the European Patent application gazette poly (hydroxy acid) react to the coupling molecule chosen from the following compound group further after a dehydrating condensation reaction is indicated, A polybasic acid anhydride, annular aminoester, annular imino ether, aromatic hydroxycarboxylic acid, a poly amino compound, polyhydric alcohol, an epoxy compound, a polyfunctional aziridine compound, lactam, lactone, ethylene glycol screw chloroformate. However, since the method currently indicated by these gazettes needs use of at least one sort of organic solvents, the influence which is not preferred is brought about from a viewpoint of an environmental problem.

[0005]

In order to use a solvent for the following reaction process, from a viewpoint of attaining the desired drying effect by an efficient method from a reaction medium, for example, it must be made to have to dry by using a drier, and the water generated during a dehydrating condensation reaction must be dried. Or a dry solvent fresh during a reaction must be added and this is not dramatically desirable from an

economic viewpoint only from a viewpoint of an environmental problem. Another problem which uses an organic solvent during a dehydrating condensation reaction is having to make it catch and dry from a solvent by using nonsolvent [as opposed to / generally / polymer for the manufactured polymer]. Such a process needs an excessive labor, and it is waste of time, and reduces the yield of the usually used raw material, and reduces further the advantage on industry, and the advantage on an environmental problem.

[0006]

In the U.S. Pat. No. 5434241 specification, the method of obtaining star-like (star-shaped) polymer is written by carrying out the polycondensation of the lactic acid under existence of the poly hydroxyl compound which has at least four hydroxyls. Although the poly (lactic acid) obtained has molar mass higher than the polymer obtained by the conventional drying method, there is a problem that there is a limit clear to the molar mass which can be attained in such a known method. When using a poly hydroxyl compound so much, in order for polymer to have hydroxyl at the end, a dehydrating condensation reaction is not continued, but, as a result, polymer with low molar mass is obtained. On the other hand, when there is very little amount of the poly hydroxyl compound used, the polymer which the effect of a poly hydroxyl compound is reduced, and a polycondensation reaction becomes being the same as that of the case where a poly hydroxyl compound does not exist, and has high mass as a result cannot be obtained.

[0007]

In European Patent gazette EP-A-0792901. It is polymer prepared by carrying out dehydration condensation of the aliphatic series diol to aliphatic dicarboxylic acid under existence of aliphatic series mono- hydroxycarboxylic acid, and the linear aliphatic polyester copolymer which has molar mass high practically enough is indicated.

[0008]

By using diisocyanate, bis-epoxide, bis-oxazoline, or bis-ortho ester for a U.S. Pat. No. 5470944 specification, By combining telechelic poly (lactic acid) polymer with low molar mass, the manufacturing method of the resolvability poly (lactic acid) copolymer with high molar mass is indicated.

[0009]

In European Patent gazette EP-A-0829503. By a dehydrating condensation reaction, the following constituent (A): (A) hydroxycarboxylic acid by which resolvability polymer containing - (C) and a manufacturing method (yield: less than 90%) for the same are indicated, (B) A polyfunctional center compound [hydroxyl content compound which has a carboxylic acid group which has three or more functionality and/or its acid anhydride, or three hydroxyls or more], and the polyfunctional compound which has a functional group beyond (C)2 **. In the desirable mode, the organic solvent is used in at least some processes of a manufacturing process. As mentioned above, there are some inconvenient problems in use of an organic solvent also from a viewpoint economical not only from a viewpoint of an environmental problem. Since all the compounds, i.e., A, B, and C are added simultaneously preferably according to this Patent Gazette, though polymer with high molar mass is obtained, there is a problem that a reaction is uncontrollable. In this Patent Gazette, another mode which may be able to control a chemical reaction correctly is also indicated.

[Description of the Invention]

[Problem(s) to be Solved by the Invention]

[0010]

This invention is made in order to solve many above-mentioned problems in the field concerned.

[Means for Solving the Problem]

[0011]

When using a specific functional center compound for a surprising thing, an artificer of this application, By the improving method by a dehydrating condensation reaction which can control by high accuracy the chemicals characteristic of polymer which is high yield and is moreover obtained. Polymer which has high molar mass is prescribed by here where it studied that letter polymer of super-branching with

high molar mass was obtained as polymer which has at least 30000g/mol of weighted mean molar mass of 50000 g/mol at least more preferably. Although a maximum of weighted mean molar mass is not restrictive, preferably and it is 1 million. A manufacturing method of polymer by this invention includes combining the 2nd prepolymer that has the 1st prepolymer and at least two functional end groups which have at least three functional end groups by a dehydrating condensation reaction between these end groups of these prepolymers.

[0012]

The following point is illustrated as an improvement point by this invention. :

(1) Since a number and/or molar mass of an arm of an organic-functions-ized prepolymer can be correctly adjusted with selection of a main starting compound, and/or its amount used, It can adjust by a method of a request of letter polymer of super-branching obtained, especially the poly (hydroxycarboxylic acid) characteristic.

(2) A letter copolymer of super-branching, for example, block copolymer, or a random copolymer can be prepared by an exact method of having been controlled which can be used in order to, obtain polymer which has a hydrophobic part and a hydrophilic portion for example.

(3) It is a functional end group in letter polymer of super-branching, and the number of end groups which can be used for another chemical reaction by request can adjust even a desired level easily.

(4) Even if an organic solvent or a coupling component is not used for letter polymer of super-branching with high molar mass, it can be prepared with high yield, and this is advantageous also not only from a viewpoint of an environmental problem but an economic viewpoint.

[0013]

According to this invention method, it became clear that biodegradability and/or hydrolytic polymer, especially poly (hydroxycarboxylic acid) (lactic acid), for example, poly, could be manufactured. From a viewpoint of an environmental problem, biodegradability and/or hydrolytic polymer are advantageous. It is because this kind of polymer does not contribute to environmental pollution and can be used for a biological system, for example, medical devices.

[0014]

As for a dehydrating condensation reaction, it is preferred to carry out water to generate to removing from a reaction medium in the state of melt at a sufficiently high temperature. However, from a viewpoint in which a pyrolysis under dehydrating condensation reaction and/or a side reaction carry out occurrence avoidance, less than 250 °C of reaction temperature is more preferably maintained by less than 230 °C. In order to remove water more efficiently, inactive gas for decompression and/or assistance is used. However, there are no special restrictions in a practice of a dehydrating condensation reaction in this invention.

[0015]

Generally a catalyst known in the field concerned in a dehydrating condensation reaction is used in a suitable quantity, and there are no special restrictions also about a use [of a catalyst in this invention, or a catalyst mixture], and addition time of a catalyst. Inorganic matter, an organic compound, acid, etc. (for example, triflic acid (triflic acid), p-toluenesulfonic acid, etc.) of metal (for example, Sn, Zn, Fe, aluminum, etc.) are contained in a typical catalyst. The amount of catalyst used is not restrictive in particular, either, as long as the desired end of flume cariosity intermediation to which reaction velocity is made to increase is attained, but generally based on quantity of a reaction reagent, 0.001 to 1% of the weight (generally 0.01 to 1 % of the weight) of a catalyst is added during the time of a reaction start of a dehydrating condensation reaction, or a reaction.

[0016]

Polymer with high molar mass can be prepared without according to this invention method, originating in the viscosity characteristic of a reaction mixture and needing an organic solvent. However, an organic solvent, for example, alcohol, ester, ether, hydrocarbon, a halogenation solvent, etc. can be used by request. The 1st and/or the 2nd prepolymer are at least 500, and are at most 50000 and poly (hydroxycarboxylic acid) which has the weighted mean molar mass of at most 500000 most preferably preferably.

[0017]

The 1st and/or a functional end group of the 2nd prepolymer are mutually chosen from functional groups (for example, a hydroxy group, a carboxyl group, a cyano group, an amide group, an epoxy group, an acid anhydride group, etc.) which can carry out a condensation reaction independently.

The 1st and/or a functional end group of the 2nd prepolymer are preferably chosen from a hydroxy group and a carboxyl group mutually independently.

[0018]

According to the desirable mode of this invention, it is polymer of biodegradability and/or hydrolysis nature. A poly (hydroxycarboxylic acid) prepolymer (prepolymer 1) and two functional end groups or more which have three or more functional end groups (for example, a carboxyl group or hydroxyl). This polymer containing a poly (hydroxycarboxylic acid) prepolymer (prepolymer 2) which has (for example, a carboxyl group or hydroxyl) is provided. Letter poly of super-branching (hydroxycarboxylic acid) which has the high molar mass by this invention by a dehydrating condensation reaction of these prepolymers (the prepolymer 1 and prepolymer 2) is obtained.

[0019]

According to this invention, any carboxylic acid which has many reactant carboxylic acid groups rather than known three or it in the field concerned can be used for preparation of a prepolymer (prepolymer 1) which has a carboxyl group at the end. :1,3,5-trimethyl 1,3,5-cyclohexane tricarboxylic acid in which the following are illustrated as this kind of carboxylic acid, 1,2,3-propane tricarboxylic acid, 1,2,3,4-cyclopentane tetracarboxylic acid, 1,2,4,5-benzenetetracarboxylic acid, 1,2,3,4-butanetetracarboxylic acid, and 1,2,3,4,5,6-cyclohexane hexacarboxylic acid.

[0020]

According to this invention, any alcohol which has many hydroxyls rather than known three or it in the field concerned can be used for preparation of a star-like prepolymer (prepolymer 1) which has hydroxyl at the end. :1,3-propanediol as which the following are illustrated as this kind of alcohol, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol, 1,7-heptane diol, 1,8-octanediol, trimethylolethane, trimethylolpropane, butanetriol, a phloroglucinol, erythritol, pentaerythritol, and dipentaerythritol. By request, alcoholic sugars which exist naturally, for example, hexose, mono- of pentose, di-, TORISAKKARIDO or maltitol, sorbitol, mannitol, xylitol, inositol, etc. can be used.

[0021]

According to the above-mentioned explanation, a telechelic prepolymer of hydroxycarboxylic acid in which an end group denaturalized is obtained by making a main functional compound react to hydroxycarboxylic acid. Subsequently, letter polymer of super-branching with high molar mass is obtained by combining a hydroxycarboxylic acid prepolymer in which this end group denaturalized with a hydroxycarboxylic acid prepolymer in which another end group denaturalized. As given an outline previously, this reaction process may be performed without using a coupling agent or a solvent.

[0022]

Alcohol and carboxylic acid which have many functional hydroxyls or carboxylic acid groups rather than two or it are called a start compound in this invention. This is because this kind of compound adjusts final molar mass and an end group of a prepolymer (the prepolymer 1 and prepolymer 2), although this alcohol and/or carboxylic acid are not necessarily contained in a start of a reaction.

Although a start compound can be used alone, it can be used also as a mixture with one sort which has the same functionality, or two or more sorts of another start compounds. When it exists by cubic shape voice from which a start compound differs (in for example, the case of inositol including nine sorts of stereoisomeric forms), one sort of isomers may be used independently, or an isomeric mixture may be used.

[0023]

A functional compound used as a start compound in this invention, It must not be either of the compounds which has two or more hydroxyls or carboxylic acid groups which were illustrated previously, It is clear that a compound containing another compound or other start nature chemical species (for example, an amide group, an amino group, an epoxy group, a cyano group, a nitro group,

the Sour Fano group, a sulfhydryl group, a siloxy group, a phosphoro basis, etc.) which have hydroxyl or a carboxylic acid group may be included.

[0024]

Hydroxycarboxylic acid which can be used in this invention is carboxylic acid which has hydroxyl in a molecule, for example, lactic acid, glycolic acid, 4-hydroxybutyrate, 6-hydroxycaproic acid, etc. are mentioned. Hydroxycarboxylic acid may be used alone or may be used together with other hydroxycarboxylic acid. When it exists by cubic shape voice from which hydroxycarboxylic acid differs (in for example, the case of lactic acid), one sort of isomers may be used alone, or it may be used as a mixture of an isomer.

[0025]

In a mode which should observe this invention method, many prepolymers combine with Example 7 rather than two, for example like a statement.

[0026]

At least one of the prepolymers is a polycondensation or hydroxy acid (preferably) of 1 or two or more amino acid, for example like a statement in the Example 8. It is preferred to obtain according to a polycondensation of hydroxy acid chosen from lactic acid, hydroxycaproic acid, hydroxybutyric acid, and glycolic acid.

[0027]

In another desirable mode, at least one of the prepolymers. For example, a compound which has structure like a ring like a dimer of hydroxycarboxylic acid (for example, lactide, glucoside), ester (for example, beta propiolactone.) which has structure like other rings delta-valerolactone, lactone like epsilon-caprolactone, bis-lactone (for example, compound which is written in a U.S. Pat. No. 3072680 specification (preferably)) L,L-lactide, D,D-lactide, racemic lactide, meso lactide, and/or glycolide. It is obtained by ring opening polymerization of cyclic ester chosen from epsilon-caprolactone, ester (for example, cyclic carbonate, preferably trimethylene carbonate) which has structure like other rings, or cyclic amide (preferably caprolactam).

[0028]

Ester, ester amide, or amide which has structure like a ring can be used together with ester which may use it alone or has structure like other rings. When it exists by cubic shape voice from which ester which has structure like a ring differs (in for example, the case of lactide), an isomer may be used alone or may be used as an isomeric mixture.

[0029]

As long as a functional end group required since there is no restriction in particular about a ring-opening-polymerization method, a dehydrating condensation reaction of a prepolymer is performed in this invention and letter polymer of super-branching is obtained is obtained, Which method (for example, method of polymerizing the extrusion-molding inside of a plane) of being known in the field concerned is applicable. As for ring opening polymerization, in a molten state which enables sufficient mixing under reaction, it is preferred to carry out by making a known catalyst exist in optimum dose by the field concerned. Inorganic matter of metal (for example, Sn, Zn, Fe, aluminum, etc.) and an organic compound, acid (for example, triflic acid, p-toluenesulfonic acid, etc.), etc. are illustrated by typical catalyst. Especially as long as the desired end of a catalyst or a catalyst mixture making reaction velocity increase is attained, it is not restrictive at the amount [of catalyst used], and addition time of a catalyst. The general amount of catalyst used is 0.001 to 1 % of the weight (generally 0.01 to 1 % of the weight) based on quantity of a reaction reagent to be used.

[0030]

This invention relates also to letter polymer of super-branching obtained by an above-mentioned method. As for this polymer, it is preferred to have biodegradability and/or a hydrolytic ester group. In a specific mode, letter polymer of super-branching by this invention is a copolymer which has a block structure, random structure, mutual structure, or graft structure, and any polymer which has such structures originates in the characteristic structure. An advantage is brought about in respect of a decomposition form, compatibility, impact strength, etc.

[0031]

The characteristic of polymer prepared by this invention, In order to make the characteristic for a predetermined use suit, to 1 or two or more polymer by this invention 1 or two or more additive agents. It can adjust further by mixing many mixtures rather than other additive agents like (for example, a filler, a reinforcing agent, a plasticizer, and stabilizer) or a color pigment, a release agent, or fire retardant, these two sorts, or it.

[0032]

A filler to be used may be which an inorganic or organic filler, For example, a gestalt of either magnesium carbonate, calcium carbonate, kaolin, tricalcium phosphate, talc, wood fibers, an apple fiber, zein, gluten casein, etc. or a filler of shape is mentioned. In this invention, it is preferred to use a natural organic filler.

[0033]

A whisker of a reinforcing agent of inorganic matter [reinforcing agent / to be used], for example, metal, and glass, textiles, a hollow fiber, a nonwoven fabric, textile fabrics, etc. are mentioned. As an organic reinforcing agent, a nonwoven fabric of textiles and natural fibers (for example, flux, a hemp, a jute, a ramie, cotton, etc.), textile fabrics, one of synthetic fibers, or a hollow fiber is illustrated.

[0034]

A suitable plasticizer, for example, monocarboxylic acid ester, polycarboxylic acid ester, polymer ester, poly alkyl ether, glycerol ester, and glycol ether may be used alone, or may be used as a mixture with other plasticizers.

[0035]

An anti-oxidant and a catalyst quencher are illustrated as suitable stabilizer. As an additive agent, a nucleating agent, a color pigment, a release agent, antistat, a printing nature accelerator, and fire retardant are illustrated.

[0036]

An additional ingredient, for example, a medical-application ingredient, a conditioner, an antiseptic, and a scavenger (scavenger) may be added to poly (hydroxycarboxylic acid) during a polymerization or after a polymerization.

[0037]

This invention also provides a polymer blend which contains many letter polymer of super-branching, and the above-mentioned additive agent by request rather than two sorts or it by this invention.

[0038]

Since a possibility of adjusting a chemical presentation and the fine structure of letter polymer of super-branching by this invention is improved, the physical characteristic of this polymer can be correctly changed within large limits. As a result, a strong and upright material, a flexible flexible material, or an adhesive material can be prepared easily. If it is a person skilled in the art, it can think out about many uses of letter polymer of super-branching and use with such flexibility. As long as this polymer fills the characteristic required for a use, there are no restrictions in particular in the use. A use in package industry with an upright material preferred as such a use is illustrated.

[0039]

Letter polymer of super-branching by compounding a copolymer which combined polymer which has high Tg, for example, and polymer which has low Tg with a monomeric unit distributed block like shape or in the shape of random. For example, it may prepare so that the desirable characteristic may be shown in a use which needs an adhesive property, pliability, and/or elasticity.

[0040]

Material which comprises a hydrophilic block which was suitable for using it as gel or dispersion liquid, for example, and a hydrophobic block can be prepared by block copolymerization or multiblock copolymerization. It originates in that there are many functional end groups, and letter poly of super-branching (hydroxycarboxylic acid) may be effectively used in a medical-application way as a biocompatible mater (material which a biological activity substance combined with this polymer chemically or physically). For example, letter poly of super-branching (hydroxycarboxylic acid) used for

a medical-application way can be prepared also by using a start compound which brings about a useful effect for special biological environment for which polymer is used. Other useful uses are uses in a blend with other polymer substances, for example.

[0041]

Letter polymer of super-branching and the above-mentioned mixture, or a blend by this invention can be effectively used on a film, a molding material, textiles, particles, gel, dispersion liquid for wrapping or a solution, coating, adhesives, a chewing gum, electronic parts, or the above medical-application ways. Letter polymer of super-branching and the above-mentioned mixture, or a blend by this invention can be used effectively also because of improvement of shock resistance of 1 or two or more polymer compounds, increase of heat distortion temperature, plasticization, compatibility-izing, or adjustment of stability.

[0042]

The following un-restrictive examples and attached drawings explain this invention further.

Drawing 1 shows a typical structural formula showing an example of a prepolymer (namely, the prepolymer 1 and the prepolymer 2) used in this invention. In order to clarify, only two repeating units per arm are shown in a star-like prepolymer.

[0043]

Drawing 2 shows a typical structural formula of letter poly of super-branching (hydroxycarboxylic acid) prepared by a dehydrating condensation reaction of this prepolymer by this invention. In order to clarify, only some repeating units are shown in letter poly of super-branching (hydroxycarboxylic acid). A main functional compound (C and C' in drawing 1 and 2) shows a compound which has a reactant group which is specified in a mode from which this invention differs. R and R' in drawing 1 and drawing 2 shows an aliphatic group within a repeating unit of polymer, and brings about a poly (hydroxycarboxylic acid) repeating unit acquired from each monomeric unit which is specified in this invention. R and R' may show the same aliphatic group, or does not need to show it. n and m in drawing 1 may show the number of repeating units in a prepolymer, and may be the same integer, or may be a different integer.

[0044]

Drawing 3 is a graph which shows relation between weighted mean molar mass at a time of making a prepolymer obtained in the experiment 5, and a prepolymer obtained in the experiment 10 react, and polymerization time.

Drawing 4 is a graph which makes a prepolymer obtained in the experiment 9 of Example 1 react to a different prepolymer obtained in the experiment 1 of Example 1 (O), the experiment 2 (**), or the experiment 4 (**), and shows relation between weighted mean molar mass at the time, and polymerization time.

Drawing 5 is a graph which shows relation between weighted mean molar mass of block copolymer at a time of making a prepolymer obtained in the experiment 7 of Example 1 react to a prepolymer obtained in the experiment 13 of Example 2, and polymerization time.

[Example]

[0045]

The dehydrating condensation reaction was performed using the rotation evaporator unit provided with the homiothermal oil bath, the vacuum suction unit, and the inactive gas feed port for laboratories. In the mixer (Brabender company make W50E type mixer) which carried out the electric heating, ring opening polymerization was performed under the inert atmosphere. By request, the homiothermal oil bath for heating to the mechanical agitation machine and the predetermined polymerization temperature for laboratories for mixing was used for ring opening polymerization, and it performed it under the inert atmosphere in round-bottom glassware. All the chemical handlings, refining, and composition followed the standard experiment procedure.

[0046]

The quantity of the start compound which has a monomer (cyclic ester of hydroxycarboxylic acid or hydroxycarboxylic acid) and a carboxylic acid group added, or hydroxyl was based on calculation of the number of mols for obtaining the predetermined molar mass of the prepolymer prepared according to a

standard polymerization procedure.

The GPC (gel permeation chromatography) device was used for measurement of molar mass. NMR (nuclear magnetic resonance) determined the presentation of the copolymer. The thermal characteristic was measured using the differential scanning calorimetry (DSC). Analysis was conducted in accordance with the known standard method in the field concerned.

[0047]

Example 1

Preparation of the prepolymer by a dehydrating condensation reaction

The start compound which has different hydroxycarboxylic acid (refer to Table 1), carboxylic acid group, or hydroxyl containing free water, And having put in the first tin (0.1 % of the weight) of 2-ethylhexanoic acid in the round bottom flask, and agitating a mixture in a rotation evaporator unit, by heating under decompression, free water was removed from the reaction mixture and low polymerization-ization of hydroxycarboxylic acid was performed. After free water of computational complexity was removed and a certain amount of low polymerization-ization was performed, the rotation evaporator unit was washed using acetone, it decompressed to the minimum pressure which a pressure is subsequently reduced gradually and is shown in Table 1, and the dehydrating condensation reaction at 180 °C was performed over time to be shown in Table 1. After interrupting a reaction, the polymerization product was cooled, and it saved under ambient conditions until it presented subsequent analysis and a ligation reaction. The conditions of a dehydrating condensation reaction and the characteristic of a prepolymer are shown in the following table 1.

[0048]

[Table 1]

表1:脱水縮合反応によって調製されたプレポリマーに対する反応条件、
モル質量およびその分布

実験 番号	ヒドロキシ カルボン酸	開始化合物	重合時間 (h)	最低圧力 (mbar)	M_w (g/mol)	M_w/M_n
1	L-乳酸	1,4-ブタンジオール	8	12	2 500	1.84
2	L-乳酸	グリセロール	8	25	3 700	1.66
3	L-乳酸	グリセロール	18	14	4 600	1.92
4	L-乳酸	ペンタエリスリトール	8	14	2 400	2.07
5 ^a	L-乳酸	イノシトール	9	20	4 700	2.02
6 ^a	L-乳酸	イノシトール	10	18	4 500	1.86
7	L-乳酸	コハク酸	14	25	3 800	2.18
8	L-乳酸	デラン二酸	13	17	3 600	4.29
9	L-乳酸	1,2,3,4,5,6-シクロヘキサンヘキサカルボン酸	8	20	2000	2.71
10	L-乳酸	1,2,3,4,5,6-シクロヘキサンヘキサカルボン酸	21	atm. ^b	1000	2.14
11 ^c	グリコール酸	グリセロール	5	30	—	—
12 ^d	グリコール酸/ L-乳酸	—	10	30	1000	2.36

^a 反応に使用した2-エチルヘキサン酸第一スズ(0.2重量%)

^b 生成水の除去を補助するために反応中で使用したアルゴンガス

^c モル質量の測定に使用した溶剤には不溶のプレポリマー。

DSC測定によれば、該プレポリマーの T_m は約180℃であった。

^d ランダム 54/46(mol/mol) コポリマー

[0049]

Example 2

Preparation of the prepolymer by ring opening polymerization

Into the reaction vessel preheated at 170 **, a monomer, a start compound, and the first tin (0.05 % of the weight) of 2-ethylhexanoic acid were introduced under the inert atmosphere. After the polymerization time set up beforehand passed, the polymerization was interrupted and polymer was cooled, and it saved under ambient conditions until it presented subsequent analysis and a ligation reaction. The characteristic of a prepolymer is shown in the following table 2.

[0050]

[Table 2]

表2:開環重合によって調製されたプレポリマーに対するモル質量およびその分布

実験 番号	モノマー	開始化合物	M_w (g/mol)	M_w/M_n
13 ^a	ε -カプロラクトン	ペンタエリスリトール	10 300	1.17
14	ε -カプロラクトン	ペンタエリスリトール	6 700	1.43
15	rac-ラクチド	フロログルシノール	33 800	1.69
16	rac-ラクチド	イソシトール	16 400	1.30
17	rac-ラクチド	ジペンタエリスリトール	21 600	1.18
18	L,L-ラクチド	ペンタエリスリトール	31 700	1.45
19 ^{b,c}	ε -カプロラクトン/ L,L-ラクチド	ペンタエリスリトール	10 200	1.24
20 ^{c,d}	ε -カプロラクトン/ L,L-ラクチド	ペンタエリスリトール	10 500	1.41
21 ^d	ε -カプロラクトン/ rac-ラクチド	ペンタエリスリトール	22 600	1.35

^a ソルベイ・インターロックス社製のポリマー^b 逐次重合によって調製されたブロックコポリマー^c 重合に使用した2-エチルヘキサン第一スズ(0.1重量)^d ランダムコポリマー

[0051]

Example 3

The relation of an increase and polymerization time of molar mass

The prepolymer (12.68g) which has at the end the carboxylic acid group obtained in the prepolymer (59.95g) and the experiment 10 which have at the end the hydroxyl obtained in the experiment 5 was introduced into the round bottom flask, and it heated at 180 **, making a mixture agitate within a rotation evaporator unit. Reduced the pressure gradually, it was made to decompress to the minimum pressure of 3mbar, and the dehydrating condensation reaction was supervised by the increase in the weighted mean molar mass as a function of polymerization time. The upright poly (hydroxycarboxylic acid) which has the weighted mean molar mass which exceeds 200000 g/mol within 10 hours was obtained. The relation between weighted mean molar mass and polymerization time is shown in drawing 3.

[0052]

Example 4

The effect of a different start compound

The prepolymer which has at the end a prepolymer of the specified quantity (40-50g) which has at the end the carboxylic acid group obtained in the experiment 9, and three sorts of different hydroxyls was introduced into the round bottom flask, and it heated at 180 **, making a mixture agitate within a rotation evaporator unit. The prepolymer which has three used sorts of different hydroxyls at the end is as follows.:

- (a) The prepolymer obtained in the experiment 1,
- (b) the prepolymer obtained in the experiment 2 -- and
- (c) The prepolymer obtained in the experiment 4.

The pressure was gradually reduced until the minimum pressure was set to 30mbars, and the dehydrating condensation reaction was supervised by the increase in the weighted mean molar mass as a function of polymerization time. In all the experiments, the prepolymer which has 100% of the weight of hydroxyl at the end based on the weight of the prepolymer which has a carboxylic acid group at the end was used. The relation between the weighted mean molar mass at the time of making it combine with the prepolymer which has at the end hydroxyl which is different in the prepolymer which has a carboxylic acid group at the end, and polymerization time is shown in drawing 4. The numerals "O", "***", and "***" in a figure show, respectively that the prepolymer which has hydroxyl at the end is obtained in the experiment 1, the experiment 2, and the experiment 4.

[0053]

Example 5

Regulation of the hydroxyl terminal group in a ligation reaction

The prepolymer (12.68g) which has at the end the carboxylic acid group obtained in the prepolymer (59.95g) and the experiment 10 which have at the end the hydroxyl obtained in the experiment 6 was introduced into the round bottom flask, and it heated at 180 **, making a mixture agitate within a rotation evaporator unit. The pressure was gradually reduced until the minimum pressure was set to 14mbars, and the dehydrating condensation reaction was supervised by the content of available -OH end group by the subsequent chemical reaction as a function of polymerization time (refer to Table 3).

[0054]

[Table 3]

表3:重合時間の関数としてのポリ(ヒドロキシカルボン酸)中の-OH末端基

重合時間(h)	-OH末端基/(mol%) ^a
0	6.9
2	6.1
4	5.7

^a NMR法によって決定した値

[0055]

Example 6

Preparation of super-branching block copolymer

The prepolymer (40.00g) which has at the end the carboxylic acid group obtained in the prepolymer (40.00g) and the experiment 7 which have at the end the hydroxyl obtained in the experiment 13 was introduced into the round bottom flask, and it heated at 180 **, making a mixture agitate within a rotation evaporator. The pressure was gradually reduced until the minimum pressure was set to 20mbars, and the dehydrating condensation reaction was supervised by the increase in the weighted mean molar mass of the block copolymer as a function of polymerization time (refer to drawing 5). within 18 hours, it has the weighted mean molar mass of 69000g/mol -- high -- modulus block copolymer was obtained.

[0056]

Example 7

Preparation of the letter random copolymer of super-branching

The prepolymer (40.00g) which has at the end the carboxylic acid group obtained in the prepolymer (40.00g) obtained in the experiment 12 and the experiment 7 was introduced into the round bottom flask, and it heated at 180 **, making a mixture agitate within a rotation evaporator unit. The pressure was gradually reduced until the minimum pressure was set to 30mbars, and the dehydrating condensation reaction was continued for 16 hours. It ranks second, [in a rotation evaporator unit] the formed polymer (10.92g). The letter random copolymer of super-branching which is tough and has flexibility was obtained by making the hydroxyl obtained in the experiment 20 under the pressure of

20mbars react to the prepolymer (16.38g) which it has at the end for 15 hours (Tg: 8 **, weighted mean molar mass:51100 g/mol).

[0057]

Example 8

Operation of the ligation reaction in a partial solid state

The prepolymer (56.18g) which has at the end the carboxylic acid group obtained in the prepolymer (24.05g) and the experiment 8 which have at the end the hydroxyl of the fine powder form acquired in the experiment 11 is put in into a round bottom flask, It heated at 180 **, making a mixture agitate within a rotation evaporator unit. Upright block copolymer including the higher glycolyl block of hydrophilic nature and the lower lactoyl block of hydrophilic nature was obtained by reducing a pressure gradually until the minimum pressure is set to 20mbars, and continuing a dehydrating condensation reaction for 33 hours. Since a glycolyl block was included, this block copolymer did not dissolve in the solvent for measurement of molar mass. DSC of the sample refined using chloroform showed a 161-198 ** broad JIMODARU (dimodal) melting peak. This can be related with melting of a different block in block copolymer.

[0058]

Example 9

Preparation of cross linked poly (hydroxycarboxylic acid)

The prepolymer (40.00g) which has at the end the carboxylic acid group obtained in the prepolymer (40.00g) and the experiment 9 which have at the end the hydroxyl obtained in the experiment 4 was introduced into the round bottom flask, and it heated at 180 **, making a mixture agitate within a rotation evaporator. The pressure was gradually reduced until the minimum pressure was set to 30mbars, and the dehydrating condensation reaction was continued for 22 hours. The obtained crosslinked polymer showed high melt viscosity, and did not dissolve it in a common organic solvent (for example, chloroform).

[Brief Description of the Drawings]

[0059]

[Drawing 1]The typical structural formula of the prepolymer used in this invention is shown.

[Drawing 2]The typical structural formula of letter poly of super-branching (hydroxycarboxylic acid) by this invention is shown.

[Drawing 3]The relation of the poly (hydroxycarboxylic acid) weighted mean molar mass and polymerization time which were acquired in Example 3 is shown.

[Drawing 4]The relation of the weighted mean molar mass of polymer and polymerization time which were acquired in Example 4 is shown.

[Drawing 5]The relation of the weighted mean molar mass of polymer and polymerization time which were acquired in Example 6 is shown.

[Translation done.]

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TECHNICAL FIELD

[Field of the Invention]

[0001]

This invention relates to letter polymer of super-branching of letter (hyperbranched) polymer of super-branching, the biodegradability which has the weighted mean molar mass (molar mass) of at least 30000 especially, and/or hydrolysis nature, and a manufacturing method for the same.

[0002]

The term of "the letter of super-branching" is a term known by the person skilled in the art of the field concerned. This term includes the polymer which has 1 or two or more central atoms as a branching off point which many polymer chains (namely, arm) combine rather than two or it which is constituted by each repeating unit. Since these arms have an additional branching off point, in the polymerization continued further, a possibility of advancing branch and/or bridge construction further is brought about.

[Translation done.]

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EXAMPLE

[Example]

[0045]

The dehydrating condensation reaction was performed using the rotation evaporator unit provided with the homoiothermal oil bath, the vacuum suction unit, and the inactive gas feed port for laboratories. In the mixer (Brabender company make W50E type mixer) which carried out the electric heating, ring opening polymerization was performed under the inert atmosphere. By request, the homoiothermal oil bath for heating to the mechanical agitation machine and the predetermined polymerization temperature for laboratories for mixing was used for ring opening polymerization, and it performed it under the inert atmosphere in round-bottom glassware. All the chemical handlings, refining, and composition followed the standard experiment procedure.

[0046]

The quantity of the start compound which has a monomer (cyclic ester of hydroxycarboxylic acid or hydroxycarboxylic acid) and a carboxylic acid group added, or hydroxyl was based on calculation of the number of mols for obtaining the predetermined molar mass of the prepolymer prepared according to a standard polymerization procedure.

The GPC (gel permeation chromatography) device was used for measurement of molar mass. NMR (nuclear magnetic resonance) determined the presentation of the copolymer. The thermal characteristic was measured using the differential scanning calorimetry (DSC). Analysis was conducted in accordance with the known standard method in the field concerned.

[0047]

Example 1

Preparation of the prepolymer by a dehydrating condensation reaction

The start compound which has different hydroxycarboxylic acid (refer to Table 1), carboxylic acid group, or hydroxyl containing free water, And having put in the first tin (0.1 % of the weight) of 2-ethylhexanoic acid in the round bottom flask, and agitating a mixture in a rotation evaporator unit, by heating under decompression, free water was removed from the reaction mixture and low polymerization-ization of hydroxycarboxylic acid was performed. After free water of computational complexity was removed and a certain amount of low polymerization-ization was performed, the rotation evaporator unit was washed using acetone, it decompressed to the minimum pressure which a pressure is subsequently reduced gradually and is shown in Table 1, and the dehydrating condensation reaction at 180 ** was performed over time to be shown in Table 1. After interrupting a reaction, the polymerization product was cooled, and it saved under ambient conditions until it presented subsequent analysis and a ligation reaction. The conditions of a dehydrating condensation reaction and the characteristic of a prepolymer are shown in the following table 1.

[0048]

[Table 1]

表1:脱水縮合反応によって調製されたプレポリマーに対する反応条件、
モル質量およびその分布

実験 番号	ヒドロキシ カルボン酸	開始化合物	重合時間 (h)	最低圧力 (mbar)	M_w (g/mol)	M_w/M_n
1	L-乳酸	1,4-ブタンジオール	8	12	2 500	1.84
2	L-乳酸	グリセロール	8	25	3 700	1.66
3	L-乳酸	グリセロール	18	14	4 600	1.92
4	L-乳酸	ペンタエリスリトール	8	14	2 400	2.07
5 ^a	L-乳酸	イノシトール	9	20	4 700	2.02
6 ^a	L-乳酸	イノシトール	10	18	4 500	1.86
7	L-乳酸	コハク酸	14	25	3 800	2.18
8	L-乳酸	デラン二酸	13	17	3 600	4.29
9	L-乳酸	1,2,3,4,5,6-シクロヘキサンヘキサカルボン酸	8	20	2000	2.71
10	L-乳酸	1,2,3,4,5,6-シクロヘキサンヘキサカルボン酸	21	atm. ^b	1000	2.14
11 ^c	グリコール酸	グリセロール	5	30	—	—
12 ^d	グリコール酸/ L-乳酸	—	10	30	1000	2.36

^a 反応に使用した2-エチルヘキサン酸第一スズ(0.2重量%)

^b 生成水の除去を補助するために反応中で使用したアルゴンガス

^c モル質量の測定に使用した溶剤には不溶のプレポリマー。

DSC測定によれば、該プレポリマーの T_m は約180℃であった。

^d ランダム 54/46(mol/mol) コポリマー

[0049]

Example 2

Preparation of the prepolymer by ring opening polymerization

Into the reaction vessel preheated at 170 **, a monomer, a start compound, and the first tin (0.05 % of the weight) of 2-ethylhexanoic acid were introduced under the inert atmosphere. After the polymerization time set up beforehand passed, the polymerization was interrupted and polymer was cooled, and it saved under ambient conditions until it presented subsequent analysis and a ligation reaction. The characteristic of a prepolymer is shown in the following table 2.

[0050]

[Table 2]

表2:開環重合によって調製されたプレポリマーに対するモル質量およびその分布

実験 番号	モノマー	開始化合物	M_w (g/mol)	M_w/M_n
13 ^a	ϵ -カプロラクトン	ペンタエリスリトール	10 300	1.17
14	ϵ -カプロラクトン	ペンタエリスリトール	6 700	1.43
15	rac-ラクチド	フロログルシノール	33 800	1.69
16	rac-ラクチド	イソシトール	16 400	1.30
17	rac-ラクチド	ジペンタエリスリトール	21 600	1.18
18	L,L-ラクチド	ペンタエリスリトール	31 700	1.45
19 ^{b,c}	ϵ -カプロラクトン/ L,L-ラクチド	ペンタエリスリトール	10 200	1.24
20 ^{c,d}	ϵ -カプロラクトン/ L,L-ラクチド	ペンタエリスリトール	10 500	1.41
21 ^d	ϵ -カプロラクトン/ rac-ラクチド	ペンタエリスリトール	22 600	1.35

^a ソルベイ・インターロックス社製のポリマー^b 逐次重合によって調製されたブロックコポリマー^c 重合に使用した2-エチルヘキサン第一スズ(0.1重量)^d ランダムコポリマー

[0051]

Example 3

The relation of an increase and polymerization time of molar mass

The prepolymer (12.68g) which has at the end the carboxylic acid group obtained in the prepolymer (59.95g) and the experiment 10 which have at the end the hydroxyl obtained in the experiment 5 was introduced into the round bottom flask, and it heated at 180 **, making a mixture agitate within a rotation evaporator unit. Reduced the pressure gradually, it was made to decompress to the minimum pressure of 3mbar, and the dehydrating condensation reaction was supervised by the increase in the weighted mean molar mass as a function of polymerization time. The upright poly (hydroxycarboxylic acid) which has the weighted mean molar mass which exceeds 200000 g/mol within 10 hours was obtained. The relation between weighted mean molar mass and polymerization time is shown in drawing 3.

[0052]

Example 4

The effect of a different start compound

The prepolymer which has at the end a prepolymer of the specified quantity (40-50g) which has at the end the carboxylic acid group obtained in the experiment 9, and three sorts of different hydroxyls was introduced into the round bottom flask, and it heated at 180 **, making a mixture agitate within a rotation evaporator unit. The prepolymer which has three used sorts of different hydroxyls at the end is as follows. :

- (a) The prepolymer obtained in the experiment 1,
- (b) the prepolymer obtained in the experiment 2 -- and
- (c) The prepolymer obtained in the experiment 4.

The pressure was gradually reduced until the minimum pressure was set to 30mbars, and the dehydrating condensation reaction was supervised by the increase in the weighted mean molar mass as a function of polymerization time. In all the experiments, the prepolymer which has 100% of the weight of hydroxyl at the end based on the weight of the prepolymer which has a carboxylic acid group at the end was used. The relation between the weighted mean molar mass at the time of making it combine with the prepolymer which has at the end hydroxyl which is different in the prepolymer which has a carboxylic acid group at the end, and polymerization time is shown in drawing 4. The numerals "O", "***", and "***" in a figure show, respectively that the prepolymer which has hydroxyl at the end is obtained in the experiment 1, the experiment 2, and the experiment 4.

[0053]

Example 5

Regulation of the hydroxyl terminal group in a ligation reaction

The prepolymer (12.68g) which has at the end the carboxylic acid group obtained in the prepolymer (59.95g) and the experiment 10 which have at the end the hydroxyl obtained in the experiment 6 was introduced into the round bottom flask, and it heated at 180 **, making a mixture agitate within a rotation evaporator unit. The pressure was gradually reduced until the minimum pressure was set to 14mbars, and the dehydrating condensation reaction was supervised by the content of available -OH end group by the subsequent chemical reaction as a function of polymerization time (refer to Table 3).

[0054]

[Table 3]

表3: 重合時間の関数としてのポリ(ヒドロキシカルボン酸)中の-OH末端基

重合時間(h)	-OH末端基/(mol%) ^a
0	6.9
2	6.1
4	5.7

^a NMR法によって決定した値

[0055]

Example 6

Preparation of super-branching block copolymer

The prepolymer (40.00g) which has at the end the carboxylic acid group obtained in the prepolymer (40.00g) and the experiment 7 which have at the end the hydroxyl obtained in the experiment 13 was introduced into the round bottom flask, and it heated at 180 **, making a mixture agitate within a rotation evaporator. The pressure was gradually reduced until the minimum pressure was set to 20mbars, and the dehydrating condensation reaction was supervised by the increase in the weighted mean molar mass of the block copolymer as a function of polymerization time (refer to drawing 5). within 18 hours, it has the weighted mean molar mass of 69000g/mol -- high -- modulus block copolymer was obtained.

[0056]

Example 7

Preparation of the letter random copolymer of super-branching

The prepolymer (40.00g) which has at the end the carboxylic acid group obtained in the prepolymer (40.00g) obtained in the experiment 12 and the experiment 7 was introduced into the round bottom flask, and it heated at 180 **, making a mixture agitate within a rotation evaporator unit. The pressure was gradually reduced until the minimum pressure was set to 30mbars, and the dehydrating condensation reaction was continued for 16 hours. It ranks second, [in a rotation evaporator unit] the formed polymer (10.92g). The letter random copolymer of super-branching which is tough and has flexibility was obtained by making the hydroxyl obtained in the experiment 20 under the pressure of

20mbars react to the prepolymer (16.38g) which it has at the end for 15 hours (Tg: 8 **, weighted mean molar mass:51100 g/mol).

[0057]

Example 8

Operation of the ligation reaction in a partial solid state

The prepolymer (56.18g) which has at the end the carboxylic acid group obtained in the prepolymer (24.05g) and the experiment 8 which have at the end the hydroxyl of the fine powder form acquired in the experiment 11 is put in into a round bottom flask, It heated at 180 **, making a mixture agitate within a rotation evaporator unit. Upright block copolymer including the higher glycolyl block of hydrophilic nature and the lower lactoyl block of hydrophilic nature was obtained by reducing a pressure gradually until the minimum pressure is set to 20mbars, and continuing a dehydrating condensation reaction for 33 hours. Since a glycolyl block was included, this block copolymer did not dissolve in the solvent for measurement of molar mass. DSC of the sample refined using chloroform showed a 161-198 ** broad JIMODARU (dimodal) melting peak. This can be related with melting of a different block in block copolymer.

[0058]

Example 9

Preparation of cross linked poly (hydroxycarboxylic acid)

The prepolymer (40.00g) which has at the end the carboxylic acid group obtained in the prepolymer (40.00g) and the experiment 9 which have at the end the hydroxyl obtained in the experiment 4 was introduced into the round bottom flask, and it heated at 180 **, making a mixture agitate within a rotation evaporator. The pressure was gradually reduced until the minimum pressure was set to 30mbars, and the dehydrating condensation reaction was continued for 22 hours. The obtained crosslinked polymer showed high melt viscosity, and did not dissolve it in a common organic solvent (for example, chloroform).

[Translation done.]

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CLAIMS

[Claim(s)]

[Claim 1]

It is a manufacturing method of letter polymer of super-branching which has the weighted mean molar mass of at least 30000, This manufacturing method including combining the 2nd prepolymer that has the 1st prepolymer and at least two functional end groups which have at least three functional end groups by a dehydrating condensation reaction between these functional end groups in these prepolymers.

[Claim 2]

A way according to claim 1 letter polymer of super-branching is biodegradability and/or hydrolysis nature.

[Claim 3]

A way according to claim 1 or 2 letter polymer of super-branching is poly (hydroxycarboxylic acid).

[Claim 4]

A way according to claim 3 letter polymer of super-branching is polylactic acid.

[Claim 5]

A way according to any one of claims 1 to 4 letter polymer of super-branching has the weighted mean molar mass of at least 50000.

[Claim 6]

A way according to any one of claims 1 to 5 letter polymer of super-branching has the weighted mean molar mass of at most 1 million.

[Claim 7]

They are a molten state or the method according to any one of claims 1 to 6 of performing by a solid state at least selectively about a dehydrating condensation reaction.

[Claim 8]

A method according to any one of claims 1 to 7 of manufacturing letter polymer of super-branching without using an organic solvent.

[Claim 9]

A way according to any one of claims 1 to 8 the 1st and/or the 2nd prepolymer are poly (hydroxycarboxylic acid) which has the weighted mean molar mass of at least 500.

[Claim 10]

A way according to any one of claims 1 to 9 the 1st and/or the 2nd prepolymer are poly (hydroxycarboxylic acid) which has the weighted mean molar mass of at most 500000.

[Claim 11]

A way according to any one of claims 1 to 10 the 1st and/or a functional end group of the 2nd prepolymer are functional groups mutually chosen from a functional group which can carry out a dehydrating condensation reaction independently.

[Claim 12]

A way according to any one of claims 1 to 11 the 1st and/or a functional end group of the 2nd prepolymer are functional groups mutually chosen from a hydroxy group and a carboxyl group

independently.

[Claim 13]

A method according to any one of claims 1 to 12 of combining many prepolymers rather than two.

[Claim 14]

A way according to any one of claims 1 to 13 at least one of the prepolymers is a prepolymer obtained by 1, a polycondensation of two or more amino acid, or a polycondensation of hydroxy acid (hydroxy acid preferably chosen from lactic acid and glycolic acid).

[Claim 15]

A way according to any one of claims 1 to 14 at least one prepolymer is a prepolymer obtained by ring opening polymerization of the following ingredient :

(1) 1 or two or more cyclic ester (preferably L,L-lactide, D,D-lactide, racemic lactide, ****- lactide and/or glycolide, epsilon-caprolactone),

(2) cyclic carbonate (preferably trimethylene carbonate) -- and/or

(3) Cyclic amide (preferably caprolactam).

[Claim 16]

A way according to any one of claims 1 to 15 at least one prepolymer is a prepolymer obtained by the reaction of a monomer and/or oligomer which have a hydroxy group, a carboxyl group, a cyano group, an amide group, an epoxy group, and/or an acid anhydride group at the end.

[Claim 17]

Subsequently, a method according to any one of claims 1 to 16 of carrying out a crosslinking process and/or a denaturation process of an end group.

[Claim 18]

Letter polymer of super-branching manufactured by a method according to any one of claims 1 to 17.

[Claim 19]

The letter polymer of super-branching according to claim 18 containing an ester group of biodegradability and/or hydrolysis nature.

[Claim 20]

The letter polymer of super-branching according to claim 18 or 19 which is a copolymer to which polymer changes from structure of the shape of block like shape, the shape of random, and alternation, or grafted state.

[Claim 21]

A mixture with an additive agent chosen from letter polymer of super-branching according to any one of claims 18 to 20 and the following group: They are many mixtures from a filler, a reinforcing agent, a plasticizer, stabilizer, a color pigment, a release agent, fire retardant and these two sorts, or it.

[Claim 22]

A polymer blend which contains many letter polymer of super-branching, and the additive agent according to claim 21 by request rather than two sorts according to any one of claims 18 to 20 or it.

[Claim 23]

The letter polymer of super-branching according to any one of claims 18 to 20, the mixture according to claim 21, Or this use [in / it is use of the polymer blend according to claim 22, and / a film, mold goods, textiles, particles, gel, dispersion liquid for wrapping or a solution, coating, adhesives, a chewing gum, electronic parts or a medical-application way].

[Claim 24]

It is use of the letter polymer of super-branching according to any one of claims 18 to 20, the mixture according to claim 21, or the polymer blend according to claim 22, This use for change of the shock resistance of 1 or two or more polymer compounds, an increase in heating deflection temperature, plasticization, reinforcement, compatibility-izing, or adjustment of stability.

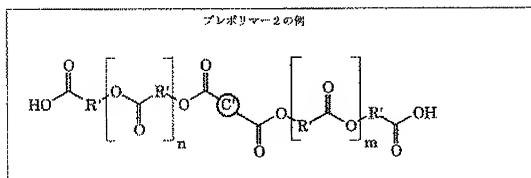
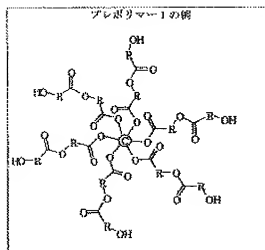


Fig. 1

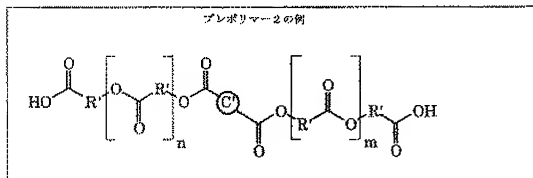
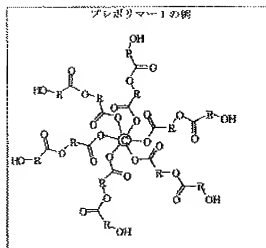


Fig. 1

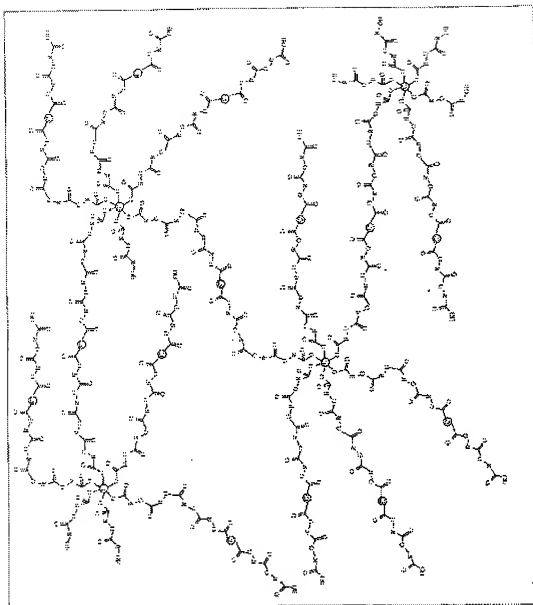


Fig. 2

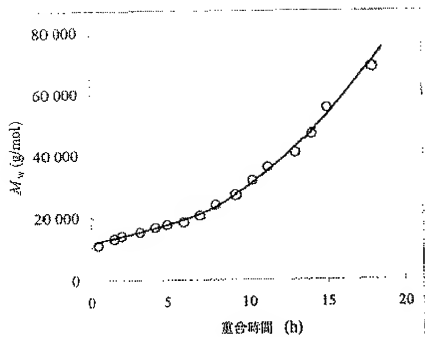


Fig. 5